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## CuSCN as Selective Contact in Solution Processed Small Molecule Organic Solar Cells Leads to over 7% Efficient Porphyrin Based Device.

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Two conjugated acceptor - $\pi$ -donor - $\pi$ -acceptor (A- $\pi$ -D- $\pi$ -A) small molecules with zinc porphyrin donor core, 3-ethylrhodanine terminal acceptors connected at meso positions by ethynylenes and linked by one or two units of thienylenevinylene denoted by **1a** and **1b**, were synthesized and their optical and electrochemical properties were investigated. The bulk heterojunction organic solar cells fabricated with **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM processed from THF exhibit power conversion efficiency of 2.75 % (J<sub>sc</sub> = 7.96 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.96 and FF = 0.36) and 3.18 % (J<sub>sc</sub> = 8.84 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.90 V and FF= 0.40), respectively. Moreover, the organic solar cells based on **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM processed from pyridine/THF solution showed PCE of 5.27 % (J<sub>sc</sub> = 10.61 mA/cm<sup>2</sup>, V<sub>oc</sub> =0.92 V and FF= 0.54) and 5.78 % (J<sub>sc</sub> = 11.58 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.86 V and FF= 0.58), respectively. But most important is the observation that the PCE was further improved to 7.24 % for devices based on **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM active layer processed with pyridine/THF solution by employing CuSCN as selective contact electrode instead of the most common hole transport material, namely PEDOT:PSS.

**Key worlds:** Porphyrin small molecules, bulk heterojunction solar cells, solvent additives, CuSCN hole transport material

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## Introduction

Solution processed organic solar cells (OSC) is a topic of current scientific interest as complementary photovoltaic technology to the current Silicon solar cells due to their solution processability, potential low cost of fabrication, lightweight and high transparency.<sup>1</sup> At present the power conversion efficiency (PCE) of solution processed organic solar cells based on single BHJ active layer using low bandgap conjugated polymer has exceed 10 %<sup>2</sup> and are expected to be higher than 11 % for tandem configuration<sup>3</sup> and more recently about 13.2 %<sup>4</sup> for triple junction organic solar cells using evaporated organic thin films. In recent years, small molecules, defined as organic molecules with low molecular weight, have attracted much attention due to the well-defined molecular structure, easier purification, and less batch to batch variations in comparison to polymers<sup>5</sup> and the PCE have been improved significantly up to 10 %, which is comparable to those of polymer counterparts.<sup>6</sup>

Porphyrins, the synthetic analogues of natural chlorophylls are of special interest, since they are known to be nature choice as light harvesting antenna systems that are involved in energy and electron transfer processes.<sup>7</sup> Porphyrins exhibit large molar extinction coefficients,<sup>8</sup> tuneable electrochemical and photophysical properties via central metal modification and/or introduction of suitable substituents at macrocycle peripheral positions.<sup>9</sup> As an example, porphyrin dyes has been successfully used as sensitizer for dye sensitized solar cells and achieved PCE more than 13 %.<sup>10</sup> In fact, in recent years, there has been a great focus of interest in the field of solution processed BHJ organic solar cells using porphyrin derivatives as donor and resulted PCEs from 2 to 8 %.<sup>11</sup> In organic solar cells the thickness limitation, imposed to obtain good carrier extraction, obliges to use molecules with outstanding light absorption. Thus, it is clear that porphyrins are a clear target for OSC.

We have previously demonstrated that molecules with a (A- $\pi$ -D- $\pi$ -A) structure, where A is the electron acceptor unit,  $\pi$  is the conjugated moiety and D is the electron donor unit, and electron withdrawing terminals is a general design rule for molecules that provide efficient solar cells. Such molecules often present: (i) high mobility with a planar structure and efficient  $\pi$ - $\pi$  interactions, (ii) a low bandgap resulting from intramolecular charge transfer and (iii) good film quality owing to a long conjugated backbone with dispersed alkyl chains similar to polymers. Herein we report the synthesis of two new conjugated A- $\pi$ -D- $\pi$ -A porphyrin small molecules, along their photophysical and electrochemical properties. These molecules consist of same thienyl substituted zinc porphyrin core as donor linked by ethynylenes to one (1a) or two (1b) units of thienylenevinylene and capped by 3-ethylrhodanine groups as acceptor units (the chemical structure is shown in Scheme 1). The ethynylenes induces molecular planarity as well as extend the  $\pi$ -system, moreover, the use of hexyl chains enhance their solubility.



Scheme 1 Structure of 1a and 1b.

During preparation of this manuscript, a porphyrin–based small molecule with similar structure to **1a**, but lacking hexyl chains in the thiophene bridge,<sup>12</sup> has been described with a power conversion efficiency up to 4.97% after processing using pyridine followed by thermal annealing. We want to remark that different alkyl chains provoke remarkable differences in solid state properties that are crucial for exciton diffusion and charge transport and consequently for the photovoltaic performance.<sup>13</sup>

These two porphyrin molecules were used as donor along with  $PC_{71}BM$  as acceptor component for the fabrication of solution processed bulk heterojunction organic solar cells and showed over all PCE of 2.75 % and 3.18 % for **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM, respectively processed with THF solution. When the active layer of device was processed with pyridine/THF solution, the photovoltaic characteristics were significantly improved resulting in PCE of 5.27 % and 5.78 %, for **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM, respectively. The enhancement in PCE was ascribed to an increase in hole mobility, resulting in better values of charge transport and charge collection rates due to the optimized crystallinity and the nanoscale morphology of the active layer, induced by the solvent additive.

Although PEDOT: PSS is widely used as hole transport layer (HTL) in most of the organic BHJ solar cells based on small molecules and polymers, due the mismatching of its work function with the HOMO energy level of the donor component in the active layer, form a barrier for hole extraction and not also a good electron blocking layer and has a tendency to trap electrons leading to change in device performance over time.<sup>14</sup> Moreover, due to the hygroscopic, acidic and protonation nature of PSS in PEDOT:PSS, influences the device stability. Copper (I) thiocyanate (CuSCN) as HTL as reported earlier for organic solar cells<sup>15</sup> and hybrid perovskite solar cells.<sup>16</sup> CuSCN is an inorganic molecular semiconductor, highly soluble in diethylsulfide and diisopropyl sulphide can be readily processed to yield thin film with high transparency across the solar spectrum and its hole mobility can be achieved up to 0.01 -0.1 cm<sup>2</sup>/Vs after the mild thermal treatment ( $\sim$ 100° C) and is compatible with a variety of organic D-A materials. In addition of desirable optical transparency, CuSCN posses a deep valence band edge  $\sim 5.30$  -5.35 eV that can help to extract the hole from the active layer as well as maximize the  $V_{oc}$ . Moreover, CuSCN can be deposited from solution using appropriate solvents and concentrations at room temperature. Inspired by the work reported in literature, we have used CuSCN as HTL to improve the PCE and achieved over all PCE around 6.59 % and 7.24 % for devices based on 1a:PC<sub>71</sub>BM and 1b:PC<sub>71</sub>BM active layer processed with pyridine/THF solutions.

**RESULTS AND DISCUSSION** 

Synthesis and characterization



Scheme 2. Synthetic route to 1a and 1b.

The synthetic approach for porphyrin based molecules **1a** and **1b** is depicted in Scheme 2, starting from the Vilsmeier formylation of 2-hexylthiophene (yield: 94%) and followed by reaction of aldehyde  $2^{17}$  with pyrrole, via a modification of Lindsey's TFA acid catalyzed condensation affording 2,2'-((5-hexylthiophen-2-yl)methylene)bis(1H-pyrrole) **3** in 77.5% yield.<sup>18</sup> Next, under Ar atmosphere, 3-(trimethylsilyl)-2-propynal was added to a solution of **3** in CHCl<sub>3</sub> and BF<sub>3</sub>.O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was added to form the porphyrinogen and this was oxidized with DDQ; after one hour, Et<sub>3</sub>N was added, affording 5,15-bis(5-hexylthiopen-2-yl)-10,20-bis((trimethylsilyl) ethynyl) porphyrin **4** in 7.3% yield. Porphyrin **4** was treated with zinc acetate in CHCl<sub>3</sub> at room temperature during one night and [5,15-bis(5-hexylthiopen-2-yl)-10,20-bis((trimethylsilyl)ethynyl)porphyrinato] zinc (**5**) was obtained in quantitative yield.<sup>19</sup> The double deprotection of the terminal triple bonds was performed by treatment of **6** with TBAF, then extracted with CHCl<sub>3</sub>, and the product was used in the following step without further purification.

Aldehydes **8a** and **8b** were obtained by double copper-free Sonogashira coupling of deprotected **6** with aldehydes **7a** and **7b**.<sup>20</sup> In the presence of  $Et_3N$  and using as catalyst  $Pd_2(dba)_3$  and triphenylarsine; compounds **8a** and **8b** where obtained in 60% yield (in both

cases) after purification by column chromatography. Finally, the target compounds **1a** and **1b** were obtained in 95% and 34% yield respectively by a double condensation of **8a** and **8b** with 3-ethylrhodanine and piperidine as base (for details, see the experimental section). All new compounds were fully characterized by FT-IR, <sup>1</sup>H- and 13C-NMR spectroscopy and MALDI-TOF mass spectrometry of **1a** and **1b** confirmed the molecular structures showing the molecular ions at 1597.27 and 2148.16 amu respectively (see ESI). Thermogravimetric analysis (TGA) results suggest that **1a** and **1b** have good stability, with decomposition temperatures (T<sub>d</sub>) above 360 °C under an N<sub>2</sub> atmosphere (see ESI, Fig. S18).

## **Optical and electrochemical properties**

The normalized optical absorption spectra of **1a** and **1b** in THF solution and as well as their thin films are shown in Fig. **1a** and **1b** and corresponding data were summarized in Table 1. Compound **1a** show a Soret band at 510 nm (lg  $\varepsilon = 5.21$ ) and a broad band at 716 nm (lg  $\varepsilon = 4.95$ ), assigned to a charge transfer transition from the porphyrin core to the 3ethylrhodanine fragment (Fig. 1a). In the other hand, **1b** show two new bands at 493 nm (lg  $\varepsilon$ = 5.12) and 548 nm (lg  $\varepsilon = 5.19$ ) assigned to the  $\pi$ - $\pi$ \* transition of the conjugated oligomer, the Soret band at 510 nm (lg  $\varepsilon = 5.15$ ) and the charge transfer band at 722 nm (lg  $\varepsilon = 5.20$ ) (Fig.1b).

|    | $\lambda_{max} \ soln$ | log  | $E^{1}_{ox}{}^{b, c}$ | $E^{1}_{red}$ | $E_{\text{HOMO}}^{d}$ | E <sub>LUMO</sub> | $E_g^{f}$ |
|----|------------------------|------|-----------------------|---------------|-----------------------|-------------------|-----------|
|    | (nm)                   | (3)  | (V)                   | (V)           | (eV)                  | ° (eV)            | (eV)      |
| 1a | 511                    | 5.21 | 0.32                  | -1.48         | -5.42                 | -3.62             | 1.80      |
|    | 716                    | 4.95 |                       |               |                       |                   |           |
|    | 346                    | 4.71 |                       |               |                       |                   |           |
| 1b | 493                    | 5.17 | 0.20                  | -1.54         | -5.30                 | -3.56             | 1.74      |
|    | 510                    | 5.15 |                       |               |                       |                   |           |
|    | 548                    | 5.19 |                       |               |                       |                   |           |
|    | 723                    | 5.20 |                       |               |                       |                   |           |
|    | 1                      |      |                       |               |                       |                   |           |

 Table 1. UV-Vis Absorption and redox<sup>a</sup> data for 1a and 1b

<sup>*a*</sup> 10<sup>-5</sup> M, in THF; <sup>*b*</sup> 10<sup>-3</sup> M in ODCB-acetonitrile (4:1) versus Fc/Fc<sup>+</sup> ( $E_{ox} = 0.04$  V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, scan rate = 100 mV s<sup>-1</sup>; <sup>*c*</sup> No reversible

processes; <sup>d</sup> calculated with respect to ferrocene,  $E_{HOMO}$ : -5.1 eV; <sup>e</sup> estimated from  $E_{red}^1$ ; <sup>f</sup>  $E_g = E_{HOMO} - E_{LUMO}$ .

In thin film, the absorption maxima of both porphyrins showed redshifted and broader relative to that in solution. The redshift is more pronounced for **1a**, and it is attributed to the extended backbone of **1b** resulting in stronger intermolecular  $\pi$ - $\pi$  stacking interactions than **1a**. Such an ordering packing of small molecules is in favour for achieving high charge mobility.<sup>21</sup> The optical bandgaps estimated from the onset of absorption spectra in thin films are 1.48 and 1.44 eV, for **1a** and **1b**, respectively. The presence of 3-ethyl-rhodanine in these molecules effectively decreases the band gaps and extends their absorption into the NIR region.<sup>22</sup> The fluorescence spectra of both porphyrins showed similar emission bands at 748 nm and 750 nm respectively. The transition energy i.e. energy between the lowest vibrational ground state to lowest vibrational excited state (E<sub>0-0</sub>) values estimated from the intersection of absorption and emission spectra (see ESI Fig. S21) are 1.71 eV (724 nm) and 1.66 eV (744 nm) for **1a** and **1b**, respectively. The lower value of E<sub>0-0</sub> for **1b** is attributed to the increased conjugation by the additional thienylenevinylene unit.



**Fig. 1** Normalized absorption spectra of **1a** and **1b** in dilute THF solution and thin film cast from THF

HOMO and LUMO levels of these porphyrins were determined by cyclic voltammetry (Fig. S22) and Osteryoung Square Wave Voltammetry (OSWV) (Fig. S23) and are summarized in Table 1. Due to the more extended conjugation, the HOMO energy of **1b** (-5.30 eV) is higher than that of 1a (-5.42 eV), being both compatible with the LUMO of [6,6]-phenyl-C<sub>71</sub>-butyric-acid methyl ester (PC<sub>71</sub>BM) (-4.00 eV). Comparing with PC<sub>71</sub>BM used as acceptor in devices, the energy difference between the HOMO level of porphyrin compounds **1a** and **1b**, and the PC<sub>71</sub>BM LUMO level, is 1.42 eV for 1a and 1.30 eV for 1b, values which in principle allow high open circuit voltages. The E<sub>LUMO</sub> values were estimated from the reduction potential in similar way and are -3.62 eV and -3.56 eV for **1a** and **1b**, respectively. The electrochemical bandgap for **1a** and **1b** are 1.80 eV and 1.74 eV, respectively and the trend is consistent with the optical bandgap and E<sub>0-0</sub>. The deeper HOMO

energy levels of these materials are favourable to achieve the high  $V_{oc}$  of the corresponding BHJ OSCs. Moreover, the LUMO energy levels are higher than that for PC<sub>71</sub>BM (-4.0 eV) for efficient exciton dissociation, which indicates their suitability for their use as donors and PC<sub>71</sub>BM as acceptor in BHJ OSCs. Since the porphyrin core is weak donor and 3-ethyl-rhodanine is strong acceptor form a weak donor – strong acceptor configuration can provide a favourable HOMO and LUMO energy levels, as well as suitable energy bandgap, which is beneficial for the efficient photovoltaic performance of BHJ OSCs.<sup>23</sup>

## **Theoretical calculations**

Theoretical geometry and HOMO-LUMO properties of **1a** and **1b** were measured by (DFT) at the B3LYP 6-31G\* (d, p) level, in gas phase, using Gaussian 03W. The most stables geometries of **1a-b** are shown in Fig. 2. Thienylenevinylene fragments are almost coplanar with the plane described by the porphyrin ring and the triple bond, with dihedral angle of  $2.84^{\circ}$  for 1a and  $5.29^{\circ}$  for **1b**. This planarity allows an extension of the conjugation between the porphyrin and the rhodanine fragments. The hexylthiophene rings are linked to the porphyrin cage with a dihedral angle of  $69.5^{\circ}$ .



Fig. 2 Geometric structure of 1a and 1b

The theoretical distributions of the orbital coefficients of the HOMO and LUMO states (Fig. 3), shows that there exists overlapping between the HOMO and LUMO, in both molecules, favoring the HOMO-LUMO electronic transitions. The charge density of the HOMO of **1a,b** is delocalized over the porphyrin and thienylenevinylene fragments. The theoretical difference of HOMO-LUMO gap agree with the values experimentally obtained, 1.87 eV and 1.74 respectively for **1a** and **1b**.



Fig. 3 Electronic density contours and energy levels for HOMO and LUMO calculated for 1a and 1b

## **Photovoltaic properties**

The solution processed BHJ OSCs were fabricated employing these porphyrins as donors and PC<sub>71</sub>BM as acceptor with a conventional device structure of ITO/ HTM/ donor:PC<sub>71</sub>BM with different weight ratios) /Al. The active layer was spin cast from the appropriated solution. The current-voltage characteristics under illumination (AM1.5 100 mW/cm<sup>2</sup>) and incident photon to current conversion efficiency spectra of the devices processed from 1:2 weight ratio of **1a** or **1b** and PC<sub>71</sub>BM blended film are shown in Fig. 4a and 4b, respectively and the photovoltaic parameters are compiled in table 2.

The device based on 1a:PC<sub>71</sub>BM and 1b:PC<sub>71</sub>BM processed without pyridine additive showed a PCE of 2.75 % ( $J_{sc} = 7.96 \text{ mA/cm2}$ ,  $V_{oc} = 0.96 \text{ and FF} = 0.36$ ) and 3.18 % ( $J_{sc} = 8.84 \text{ mA/cm}^2$ ,  $V_{oc} = 0.90 \text{ V}$  and FF= 0.40), respectively. Both the devices showed reasonably high value of  $V_{oc}$ , due to their deeper HOMO energy levels. The higher value of value of  $V_{oc}$  for the device based on 1a as compared to 1b, attributed to the relatively deeper HOMO level

of 1a than 1b, since the  $V_{oc}$  of the BHJ OSC is directly related to the energy difference between the HOMO energy level of donor and LUMO energy level of acceptor employed in BHJ active layer. The higher value of PCE for 1b as compared to 1a mainly attributed to the superior value of J<sub>sc</sub> and FF. As shown in Fig. 4b, the IPCE spectra of the 1a:PC<sub>71</sub>BM and 1b:PC<sub>71</sub>BM based OSCs showed broad response covering from 350 nm to 850 nm, consistent with the absorption spectral properties of 1a and 1b thin films. Moreover, the device based on 1b showed slightly wider response and high values of IPCE, which is consistent with its absorption spectra. The LUMO offset between the 1b and PC<sub>71</sub>BM is larger than that for 1a and PC<sub>71</sub>BM indicates the stronger driving force for the later than former may also be the reason for higher J<sub>sc</sub> for the solar cell based on 1b.

Table 2 Photovoltaic parameters of organic BHJ solar cells based on  $1a:PC_{71}BM$  (1:2) and  $1b:PC_{71}BM$  (1:2)

| Active layer                                | $J_{ m sc}$ | V <sub>oc</sub> | FF   | PCE  | R <sub>s</sub>          | R <sub>sh</sub>         |
|---|-------------|-----------------|------|------|-------------------------|-------------------------|
|   | $(mA/cm^2)$ | (V)             |      | (%)  | $(\Omega \text{ cm}^2)$ | $(\Omega \text{ cm}^2)$ |
| $1a:PC_{71}BM^{a}$                          | 7.86        | 0.96            | 0.36 | 2.75 | 52                      | 240                     |
| <b>1b:</b> PC <sub>71</sub> BM <sup>a</sup> | 8.84        | 0.92            | 0.40 | 3.18 | 43                      | 256                     |
| <b>1a:</b> PC <sub>71</sub> BM <sup>b</sup> | 10.61       | 0.90            | 0.54 | 5.27 | 26                      | 308                     |
| <b>1b:</b> PC <sub>71</sub> BM <sup>b</sup> | 11.58       | 0.86            | 0.58 | 5.78 | 18                      | 378                     |
| $1a:PC_{71}BM^{c}$                          | 10.74       | 0.99            | 0.62 | 6.59 | 16                      | 386                     |
| <b>1b:</b> $PC_{71}BM^{c}$                  | 11.67       | 0.94            | 0.66 | 7.24 | 12                      | 412                     |

 $^a$  CB cast;  $^b$  Pyridine 3% v / THF cast;  $^c$  CuSCN HTL and active layer processed with pyridine 3% v / THF

Both, **1a** and **1b** have same chemical structure except for the thienylenevinylene conjugation length. In order to get information about the influence of conjugation length of  $\pi$  linker on the charge transport properties, hole mobility ( $\mu_h$ ) in the active layer was measured J-V characteristics in dark using a hole only device, i.e. ITO/PEDOT:PSS/active layer/Au and fitting the curves with space charge limited current model. Fig. 5 shows the J-V characteristics of the hole only devices using **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM active layers. The hole mobility estimated from the Fig. 5 and fitting with SCLC model are 7.32 x10<sup>-6</sup> cm<sup>2</sup>/Vs and 9.23 x10<sup>-6</sup> cm<sup>2</sup>/Vs for **1a** and **1b**, respectively. The hole mobility is determined by the intramolecular backbone, intermolecular packing and  $\pi$ - $\pi$  stacking. Since both the porphyrins have same molecular structure except the conjugation length of  $\pi$ -linker, therefore the difference in the hole mobility may be due to the intermolecular  $\pi$ - $\pi$  stacking. The two units of thienylenevinylene in **1b** may leads to strong intermolecular  $\pi$ - $\pi$  stacking, resulted higher

mobility than **1a**. In comparison to **1a**, **1b** showed stronger intermolecular interaction as evidenced by the redshift in the absorption in both solution and thin film, contributing to its charge transport ability.<sup>24</sup> The stronger  $\pi$ - $\pi$  stacking can increase the hole mobility due to better molecular packing.<sup>25</sup> These parameters are responsible for higher  $J_{sc}$  and FF resulting superior overall PCE for OSC based on **1b** as compared to **1a**.



**Fig. 4** (a) Current –voltage characteristics under the illumination of AM1.5 at 100 mW/cm<sup>2</sup> and (b) IPCE spectra of the BHJ OSCs based on porphyrin: $PC_{71}BM$  (1:1)



**Fig. 5** Current–voltage characteristics of hole-only devices based on active layers cast from THF and pyridine/THF solvents. The solid lines are SCLC fitting.

The overall PCE of BHJ OSCs based on these porphyrins processed with THF is smaller than reported in literature for small molecules as donor. Although the  $V_{\rm oc}$  of these devices is reasonably high, the lower PCE is mainly due low values of both  $J_{sc}$  and FF. These parameters directly related to the light harvesting efficiency of the active layer and the resulting charge generation as well as the charge transport within active layer and collection to the respective electrodes and these processes depend upon the morphology of active layer and charge mobilities. A well-defined morphology and phase separation between the donor and acceptor components in the active layer within the range of exciton diffusion lengths (~15-20 nm) are necessary for efficient exciton dissociation and charge transport.<sup>26</sup> As reported in literature, the morphology of the active layer can be controlled by the appropriate treatments of active layer i.e. thermal annealing,<sup>27</sup> solvent annealing<sup>28</sup> and solvent additives<sup>29</sup> for both polymer and small molecule solar cells. The solvent additive method has been recently adopted to improve the performance of organic solar cells based on porphyrins as donor. In order to improve the PCE of our devices we have employed solvent additive treatment method using a small amount of pyridine as solvent additive, as it is known to be more effective than other solvent additive in case for porphyrin based solar cells.<sup>30</sup> We have varied the concentration of pyridine in THF host solvent from 0.5 v% to 3.5 v% and found that 3 v % gives the best result. The J-V characteristics under illumination and IPCE spectra of the devices processed with pyridine solvent additive are shown in Fig. 4a and 4b, respectively and photovoltaic parameters are compiled in Table 2. The PCE value of the

devices with solvent additives was significantly enhanced from 2.75 % to 5.27 % ( $J_{sc} = 10.61 \text{ mA/cm}^2$ ,  $V_{oc} = 0.92 \text{ V}$  and FF= 0.54) and 3.18 to 5.78 % ( $J_{sc} = 11.58 \text{ mA/cm}^2$ ,  $V_{oc} = 0.86 \text{ V}$  and FF= 0.58) for **1a** and **1b**, respectively. The improvement in the  $J_{sc}$  is consistent with the IPCE spectra of the devices processed with solvent additive, i.e. the IPCE values are higher throughout the whole wavelength region. The calculated values of  $J_{sc}$  from the IPCE spectra were about 10.48 mA/cm<sup>2</sup> and 11.43 mA/cm<sup>2</sup> for **1a** and **1b** based devices, respectively in good agreement, within experimental error, with the values observed in the J–V characteristics of devices under illumination.

The PCE of BHJ organic solar cells, the  $J_{sc}$  is directly related to the light harvesting efficiency of the active layer, therefore, therefore, in order to get information about influence of pyridine additive on the change in light harvesting efficiency of the devices, we have recorded the UV-visible absorption spectra of the active layers with and without pyridine additive and shown in Fig. 6 for **1b**:PC<sub>71</sub>BM (1:2) thin films only. Similar results have been observed for **1a**:PC<sub>71</sub>BM (1:2) thin films. Compared to the film cast from THF, the pyridine/THF cast film shows a wide absorption and high absorption coefficient particularly to the absorption bands corresponds to porphyrin, which is related to the enhanced  $\pi$ - $\pi$ stacking. Therefore, we believe that the light harvesting efficiency have been improved with the pyridine additive, which may be one of the reasons for the improvement in  $J_{sc}$ .



Fig. 6 Normalized absorption spectra of 1b:PC<sub>71</sub>BM thin film cast from THF and pyridine/THF solutions.

The crystallinity of the active layer plays an important role in charge transport and collection, thereby affecting the overall PCE of organic bulk heterojunction. The XRD patterns of pristine 1a and 1b displayed in Fig. 7a and showed significant (100) diffraction peaks at  $2\theta = 7.26^{\circ}$  and  $7.32^{\circ}$ , respectively, resulting d-spacing of 1.52 nm and 1.48 nm, for 1a and 1b, respectively. To get information about the change in the crystallinity of porphyrin: PC<sub>71</sub>BM active layer thin films with the addition of pyridine solvent into CB, prior to spin casting, we have recorded the x-ray diffraction (XRD) pattern of the spin cast thin film from THF and pyridine/THF solutions. The **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM blends cast from THF show similar diffraction peaks with weak intensity (as shown in Fig. 7b for 1b:PC<sub>71</sub>BM), suggesting effective mixing of PC<sub>71</sub>BM and porphyrin. However, this diffraction peak becomes more intense in corresponding blend cast from pyridine/THF solvent, while the width at half maximum height is decreased. These results shows that the blend film cast from THF solvent has low crystallinity, while in the case of blend film cast from pyridine/THF solvent, the crystallinity and  $\pi$ -conjugation of porphyrin in the blend film increase. This is probably due to the difference in boiling point of THF and pyridine, which makes the film to dry slowly, assisting in the formation of better self-ordered structure of the blend. The increase in the crystallinity leads to an enhancement in light harvesting properties of active layer and higher hole mobility in the blend thin film, leading to increase in  $J_{sc}$  and FF.

Atomic force microscopy (AFM) was used to investigate the change in the surface morphology of the active layer induced by pyridine solvent additive. The AFM scans were carried out for the blend films spin coated onto ITO coated substrate using the same fabrication conditions for device fabrication. Fig. 8 shows the AFM images for **1b**:PC<sub>71</sub>BM cast with and without solvent additives and corresponding root mean square (rms) roughness are 0.98 nm and 1.82 nm, for the film cast from THF and pyridine/THF solutions, respectively. The blend cast from THF shows relatively flat and poor phase separation which is not favorable for charge transfer from porphyrin to PC<sub>71</sub>BM thus limited the PCE of resulting device. However, spin coated film from pyridine/THF showed more aggregated domains and phase separated domains with larger rms surface roughness. The aggregated domains may originate from enhanced intermolecular interaction of porphyrin, during the film formation.<sup>31</sup> A higher surface roughness is expected to increase the internal light scattering and enhance the light absorption.<sup>32</sup> The blend film with larger domain size suggests a good phase separation and well-connected domains, which allow efficient charge generation and charge transfer within the active layer.



Fig. 7 X-ray diffraction patterns of (a) 1a and 1b thin films cast from THF and (b) 1b:PC71BM



Fig. 8 AFM images of 1b:PC<sub>71</sub>BM blend films cast from THF and pyridine/THF solutions (size,  $3 \mu m \times 3 \mu m$ ).

The charge carrier mobility in the BHJ active layer is crucial for the overall PCE of the organic solar cell because the photogenerated charge carriers extract by electrodes depends on the competition between carrier sweeps out, which is limited by the mobility of charge carriers, their loss by recombination.<sup>33</sup> In order to get information about the influence of the pyridine additive on the charge carrier mobilities, we have measured the hole mobilities using the J-V characteristics of the hole only devices (Fig. 4). Fitting the experimental results with SCLC model (solid lines), the hole mobilities are found to be 3.14  $\times 10^{-5}$  cm<sup>2</sup>/Vs and 1.35  $\times 10^{-5}$  cm<sup>2</sup>/Vs for **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM processed with pyridine additive. In similar manner, we have also estimated the electron mobilities for the blends processed with and without pyridine additive and found to be in the range of 2.36- 2.48  $\times 10^{-4}$  cm<sup>2</sup>/Vs. The increase in the hole mobility and almost same electron mobility with solvent additive treatments results more balanced charge transport in the devices as compared to that for their counterpart devices processed without additive and enhances the FF and  $J_{sc}$  values, leading to higher PCE value.

We further investigated the influence of pyridine additive on the photogeneration of charge carriers in the organic solar cells based on 1a and 1b donor by investigating the variation of photocurrent  $(J_{ph})$  with effective voltage  $(V_{eff})$ . The  $J_{ph}$  value is estimated as  $J_{ph} =$  $J_{\rm L}$ - $J_{\rm D}$ , where  $J_{\rm L}$  and  $J_{\rm D}$  are the current density under illumination and dark, respectively.<sup>34</sup> The  $V_{\rm eff}$  value is determined as  $V_{\rm eff} = V_{\rm o} - V$ , where  $V_{\rm o}$  is voltage at which the  $J_{\rm ph}$  value is zero.<sup>35</sup> Therefore, the  $V_{eff}$  is corresponds to the strength of electric field within the device to extract the charge carriers. The variation of J<sub>ph</sub> with V<sub>eff</sub> is shown on Fig. 9. The log-log plot of J<sub>ph</sub> versus V<sub>eff</sub> shows to distinct regions, i.e. linear and saturation region. As observed in Fig. 9, the devices based on active layer processed without pyridine additive showed no clear saturation in J<sub>ph</sub> with increasing V<sub>eff</sub>, indicating that the internal electric field is not sufficient for charge extraction and saturation region is field dependent. However, the devices processed with pyridine additive showed clear saturation region in J<sub>ph</sub>-V<sub>eff</sub> curves indicating field independent saturation, leading to efficient charge extraction and collection. Therefore at full saturation, we assume that all the excitons generated after the absorption of photons in the active layer are dissociated into free electrons and holes and subsequently collected by the respective electrodes. We have estimated the maximum generation rate of free charge carriers  $(G_{max})$  using  $J_{phsat} = qG_{max}L$ , where,  $J_{phsat}$  is the photocurrent density at full saturation point in Fig. 9, q is the elementary charge and L is the thickness of active layer. The estimated values of G<sub>max</sub> for the devices based on 1a:PC<sub>71</sub>BM (THF cast), 1b:PC<sub>71</sub>BM (THF cast), 1a:PC<sub>71</sub>BM

(pyridine/THF cast) and **1b**:PC<sub>71</sub>BM (pyridine/THF cast) are  $1.50 \times 10^{28} \text{ m}^3 \text{s}^{-1}$ ,  $1.64 \times 10^{28} \text{ m}^3 \text{s}^{-1}$ ,  $2.13 \times 10^{28} \text{ m}^3 \text{s}^{-1}$  and  $2.34 \times 10^{28} \text{ m}^3 \text{s}^{-1}$ , respectively. The trends observed for the G<sub>max</sub> with different devices is consistent with the enhancement of J<sub>sc</sub> as well as the UV-visible absorption coefficient, indicating more efficient exciton generation and their dissociation in the active layer processed with pyridine solvent additive. The charge collection probability (P<sub>c</sub>) of the present solar cells was estimated accordingly P<sub>c</sub> = J<sub>sc</sub>/J<sub>phsat</sub> and found to be 0.62, 0.64, 0.74 and 0.78 for **1a**:PC<sub>71</sub>BM (THF cast), **1b**:PC<sub>71</sub>BM (THF cast), **1a**:PC<sub>71</sub>BM (pyridine/THF cast), respectively. The greater value of P<sub>c</sub> for the devices processed with pyridine additive based devices as compared to that for without pyridine additive, is attributed to the better phase separation in the active layer, increased hole mobility and improved balance in charge transport.



Fig. 9 Variation of photocurrent density  $(J_{ph})$  with the effective internal voltage  $(V_{eff})$  for devices processed with and without pyridine additives

We have measured the series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) from the slope of the J-V characteristics of the devices, under illumination around  $V_{oc}$  and  $J_{sc}$ , respectively and summarized in Table 2. In organic BHJ solar cell, the  $R_s$  is composed of the bulk resistance of active layer depends upon the charge transport ability within active layer and the morphology of the active layer. It can be seen from the Table 2, the  $R_s$  of the devices processed from pyridine/THF is significantly lower than that processed with THF and can be attributed to better morphology and balanced charge transport.<sup>36</sup> The increase in  $R_{sh}$  is related to the decrease in leakage current and depends on the intermolecular interaction (or electronic) coupling between the donor and acceptor materials in the active layer.



**Fig. 10** J-V characteristics of devices using CuSCN as hole transport layer for active layers processed with pyridine/THF solutions.

We have tried CuSCN as HTL as an attempt to improve the PCE of our devices. Since both **1a** and **1b** posses HOMO energy levels around in between -5.42 and -5.30 eV, there is a energy mismatch with the HOMO energy level of PEDOT:PSS (-5.0-5.1 eV) and form a barrier for hole extraction, therefore there is possibilities to improve the PCE of our present devices. As active layer we have used pyridine/CB cast film for investigation. The device fabrication is similar as described in experimental part except HTL. The J-V characteristics of the devices are shown in Fig. 10. The devices based on **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM showed PCE of 6.59 % (J<sub>sc</sub> =10.74 mA/cm<sup>2</sup>, V<sub>oc</sub> =0.99 V and FF=0.62) and 7.24 % (J<sub>sc</sub> =11.67 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.94 V and FF= 0.66), respectively, which is higher than that for the PEDOT:PSS HTL. The J<sub>sc</sub> values are almost similar that for PEDOT:PSS HTL, since the both PEDOT:PSS and CuSCN have similar transparency for visible and NIR region of solar spectrum. Replacing the PEDOT:PSS with CuSCN, the FF increases from 0.54 to 0.62 and 0.58 to 0.66 for **1a** and **1b** based devices, respectively, may related to the better Ohmic contact formation between the active layer and CuSCN, due to the deeper work function of CuSCN than PDEOT:PSS. The improvement in  $V_{oc}$  with respect to PEDOT:PSS could be explained by better alignment between the HOMO level of porphyrin donor and valance band edge of CuSCN (-5.35 eV) at the active layer/HTL interface, which act as good electron blocking layer.



**Fig. 11** Dark current density-voltage characteristics for the device using PEDOT:PSS and CuSCN HTL based on **1b**:PC<sub>71</sub>BM active layer processed with pyridine/THF solutions.

The HTL used in the organic BHJ solar cell should have ability to limit the passage of dark injected minority carriers in reverse bias from anode to cathode through active layer. To get information about this, we have measured the dark J-V characteristics of the devices based on **1b**:PC<sub>71</sub>BM active layer (Fig. 11). It can be seen from this figure that the current density at 0.47 V in reverse bias for PEDOT:PSS and CuSCN HTL is 0.0012 mA/cm<sup>2</sup> and 0.00016 mA/cm<sup>2</sup>, respectively and higher rectification ratio for CuSCN as compared to PEDOT:PSS, indicating that CuSCN indeed suppress the minority charge carrier injection into the active layer, thus reducing the recombination process. Moreover, by fitting the experimental J-V characteristics in dark with Mott-Gurney relationship, we estimated that V<sub>bi</sub> value for CuSCN is 0.098 V higher than that for PEDOT:PSS. The shunt resistance has also been higher for CuSCN as compared to PEDOT:PSS. The above observations have synergetic effect on the ability to collect holes and eventually improve the V<sub>oc</sub>, FF and PCE.

We have also estimated the  $P_c$  for these devices using the variation of  $J_{ph}$  with  $V_{eff}$  (Figure 12). As shown in Figure 12, the  $J_{ph}$  tends to saturate at lower  $V_{eff}$  as compared to the counterpart devices based on PEDOT:PSS. The values of  $P_c$  for the devices based on 1a and 1b are about 0.85 and 0.88, respectively. These values are higher than that for devices based on PEDOT:PSS, indicating that employing CuSCN the better Ohmic contact is formed and extract the hole more efficiently, leading to suppress the charge recombination and increase in FF. As the  $V_{eff}$  corresponds to the internal voltage to extract the charge carriers, with the CuSCN low internal voltage is needed to sweep out the charge carriers.

Moreover, the R<sub>s</sub> and R<sub>sh</sub> has been decreased and increased, respectively for the CuSCN HTL relative to PEDOT:PSS also an indicative to reduced charge recombination and efficient charge extraction.



Fig. 12 Variation of photocurrent density  $(J_{ph})$  with the effective internal voltage  $(V_{eff})$  for devices processed with pyridine/THF solvent and using CuSCN as HTL.

### CONCLUSIONS

In this article, we report the synthesis and optical and electrochemical properties of two new conjugated acceptor- $\pi$ -donor- $\pi$ -acceptor (A- $\pi$ -D- $\pi$ -A) small molecules with zinc porphyrin donor core 3-ethylrhodanine terminal acceptors connected at *meso* positions by ethynylenes and linked by one (**1a**) or two (**1b**) units of thienylenevinylene. The optical and

electrochemical properties of these two porphyrins suggest that blend films these with PC<sub>71</sub>BM can effectively harvest the photons from visible to NIR region of solar spectrum and transfer the electrons from porphyrins to PC<sub>71</sub>BM, resulting in photovoltaic response. The BHJ solar cells from 1a:PC<sub>71</sub>BM and 1b:PC<sub>71</sub>BM processed from THF displayed PCE of 2.75 % and 3.18 %, respectively. In order to improve the PCE further, we have spin cast the active layers from pyridine/CB solvent and found that the overall PCE has been significantly enhanced up to 5.27 % and 5.78 %, for 1a:PC71BM and 1b:PC71BM based devices, respectively, as a result of higher values of  $J_{sc}$  and FF and are related to the exciton generation/separation into free charge carrier and mobility/ charge transport which are found to be improved by the morphology/crystallinity of the active layer, induced by pyridine solvent additive. Moreover, the PCE has been improved further up to 6.59 % and 7.24 % for **1a**:PC<sub>71</sub>BM and **1b**:PC<sub>71</sub>BM active layer processed with pyridine/THF solution by employing the CuSCN HTL. The increase in the PCE is due to the suppression on injection of minority carries (electrons) from anode and increase in V<sub>bi</sub> relative to PEDOT:PSS based devices. Moreover, the low internal field is sufficient to sweep out the charge carriers and reduce the recombination.

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### **EXPERIMENTAL**

2,2'-((5-hexylthiophen-2-yl)methylene)bis(1H-pyrrole) (3). At room temperature and under argon atmosphere, 0.08 mL of TFA (7.71  $\mu$ L/mmol) was added to a solution of **2Error! Reference source not found.** (2.00 g, 10.2 mmol) and pyrrol (4.17 mL, 60 mmol). The solution was stirred at room temperature for 30 min before quenching with trimethylamine (1 mL). The organic phase was extracted with chloroform (3 x 50 mL), dried over MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure and the crude was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>, 1:1). The final product was light brown oil (7.88 mmol, 2.46 g, 77.5% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 7.93 (s, 2H), 6.89 (s, 2H) 6.64 (d, 4H, J = 3.3 Hz), 6.21 (dd, 2H, H = 2.8 Hz, J = 5.5 Hz), 6.09 (s,

2H), 5.66 (s, 1H), 2.79 (t, 2H, J = 7.6 Hz), 1.68 (q, 2H, J = 7.6 Hz), 1.42-1.35 (m, 6H), 0.95 (t, 3H, J = 6.5 Hz). FT-IR (ATR)  $\nu/\text{cm}^{-1}$ : 3390, 2920, 2850, 1690, 1560, 1460, 1430, 1250, 1110, 1090, 1030, 968, 883, 760, 714.

5,15-bis(5-hexylthiopen-2-yl)-10,20-bis((trimethylsilyl)ethynyl)-porphyrin (4). In anaerobic conditions, 3-(trimethylsilyl)-2-propynal (0.98 mL, 6.62 mmol) and boron trifluoride diethyl etherate (BF<sub>3</sub>O·Et<sub>2</sub>O, 3.3 mM, 0.27 mL, 2.18 mmol) were added to a solution of 3 (2.00 g, 6.6 mmol) in 660 mL of CHCl<sub>3</sub>, and the solution was stirred at room temperature for 45 min before adding DDQ (1.13 g, 4.96 mmol). The solution was stirred at room temperature for 1 hour before quenching with 1.3 mL of Et<sub>3</sub>N (0.4 mL/mmol). After 30 min, the solvent was removed under reduced pressure. The crude was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>:toluene, 7:2.8:0.2). The final product was a green-purple solid (0.23 mmol, 200 mg, 7.3% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 9.6 (d, 4H, J = 4.6 Hz), 9.11 (d, 4H, J = 4.6 Hz), 7.69 (d, 2H, J = 3.2 Hz), 7.19 (d, 2H, J = 3.2 Hz), 3.14 (t, 4H, J = 7.54 Hz), 2.01-1.93 (m, 4H), 1.6-1.58 (m, 6H), 1.48-1.46 (m, 8H), 1.00 (t, 4H, J = 6.9 Hz), 0.62 (s, 18H), -2.13 (m, 2H). MALDI-TOF MS (m/z): calculated: 834.36; found: 835.60 (M<sup>+</sup>). FT-IR (ATR) v/cm<sup>-1</sup>: 3310, 2950, 2920, 2850, 2140, 1550, 1470, 1370, 1340, 1250, 1140, 1060, 984, 949, 837, 795, 756, 698, 617.

**Compound 5**. To a solution of **4** (0.18 mmol, 150 mg) in 15 mL of CHCl<sub>3</sub> (85 mL/mmol), and 0.5 mL of MeOH (2.5 mL/mmol) zinc acetate (165 mg, 0.9 mmol) was added and the solution was stirred at room temperature during four hours. Then, the organic phase was extracted with CHCl<sub>3</sub> (3 x 25mL), dried and the solvent was removed under reduced pressure. The crude was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>, 1:1) affording compound **5** as a green-purple solid (0.17 mmol, 160 mg, 99.1 % yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.6 (d, 4H, J = 4.6 Hz), 9.18 (d, 4H, J = 4.6 Hz), 7.69 (d, 2H, J = 3.2 Hz), 7.19 (d, 2H, J = 3.2 Hz), 3.14 (t, 4H, J = 7.54 Hz), 2.01-1.93 (m, 4H), 1.64-1.60 (m, 6H), 1.48-1.47 (m, 6H), 1.00 (t, 6H, J = 6.9 Hz), 0.62 (s, 18H). MALDI-TOF MS *(m/z)*: calculated for C<sub>50</sub>H<sub>56</sub>N<sub>4</sub>S<sub>2</sub>Si<sub>2</sub>Zn: 896.28; found: 896.63 (M<sup>+</sup>). FT-IR (ATR) v/cm<sup>-1</sup>: 2920, 2850, 2140, 1490, 1460, 1340, 1300, 1250, 1210, 1160, 1060, 1000, 972, 837, 791, 756, 710, 621.

**Compound 6.** At room temperature and under argon atmosphere, TBAF (1M in THF, 0.4 mL, 0.4 mmol) was added to a solution of **5** (150 mg, 0.16 mmol) in 35 mL of CHCl<sub>3</sub> (220 mL/mmol). It was added to the solution. The solution was stirred at room temperature for 3 hours and then CaCl<sub>2</sub> (222 mg, 2 mmol) was added. After stirring for 30 min, the organic phase was extracted with CHCl<sub>3</sub>, (3 x 50 mL). The resultant organic phase was dried, the

solvent was removed under reduced pressure and deprotected **6** was obtained as a blue-green solid, and used in the next synthetic step without further purification.

## Synthesis of 8a.

Using the procedure previously described for Sonogashira condensation,<sup>20</sup> to a solution of deprotected **6** (200 mg, 0.27 mmol) and **7a**,<sup>20</sup> (337 mg, 0.8 mmol) in 40 mL of THF and 7.5 mL of Et<sub>3</sub>N, was added a mixture of Pd<sub>2</sub>(dba)<sub>3</sub> (152 mg, 0.16 mmol) and AsPh<sub>3</sub>, (340 mg, 1.1 mmol). The crude was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>, 2:3) and recrystallized with CH<sub>2</sub>Cl<sub>2</sub>:MeOH. The final product was a turquoise solid (0.16 mmol, 218 mg, 60 % yield). **8a:** <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.56 (s, 2H), 9.07 (d, 4H, J = 4.6 Hz), 8.91 (d, 4H, J = 4.6 Hz), 7.76 (d, 2H, J = 3.2 Hz), 7.28 (d, 2H, J = 3.2 Hz), 3.23 (t, 4H, J = 7.6 Hz), 2.47 (s, 2H), 2.30 (s, 2H), 2.10-2.03 (m, 4H), 1.74-1.66 (m, 4H), 1.6-1.52 (m, 20H), 1.38-1.33 (m, 12H), 1.30-1.26 (m, 8H), 1.07-1.03 (t, 4H, J = 6.9 Hz), 0.92-0.87 (m, 18H). MALDI-TOF MS (*m*/*z*): calculated for C<sub>78</sub>H<sub>92</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub>Zn: 1308.54; found: 1309.01 (M<sup>+</sup>). FT-IR (ATR) v/cm<sup>-1</sup>: 2920, 2850, 2180, 1650, 1610, 1490, 1450, 1410, 1290, 1210, 976, 791, 733, 710, 667.

# Synthesis of 8b.

Using the general procedure for Sonogashira condensation previously described, to a solution of deprotected **6** (125 mg, 0.17 mmol) and **7b**<sup>20</sup> (300 mg, 0.5 mmol) in 40 mL of THF (230 mL/mmol) and 7.5 mL of Et<sub>3</sub>N (45 mL/mmol), was added to a mixture of Pd<sub>2</sub>(dba)<sub>3</sub> (92 mg, 0.1 mmol) and AsPh<sub>3</sub>, (205 mg, 0.7 mmol). The crude was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>, 2:3) and recrystallized with CH<sub>2</sub>Cl<sub>2</sub>:MeOH. The final product was a turquoise solid (0.10 mmol, 374 mg, 60 % yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.59 (s, 2H), 9.29 (d, 4H, J = 3.9 Hz), 9.12 (d, 4H, J = 3.9 Hz), 7.75 (s, 2H), 7.25 (s, 2H), 7.05 (d, 2H, J = 16 Hz), 6.76 (d, 2H, J = 16 Hz), 3.21 (t, 3H, J = 7.14 Hz), 2.73 (s, 3H), 2.57 (d, 6H, J = 21.8 Hz), 2.40 (s, 3H), 2.04 (t, 3H, J = 6.9 Hz), 1.77 (s, 2H), 1.65-1.63 (m, 6H), 1.5-1.26 (m, 68H), 1.05-0.99 (m, 16H), 0.94-0.89 (m, 20H). MALDI-TOF MS *(m/z)*: calculated for C<sub>114</sub>H<sub>148</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>Zn: 1860.92; found: 1862.30 (M<sup>+</sup>). FT-IR (ATR) v/cm<sup>-1</sup>: 2920, 2850, 2170, 1650, 1590, 1490, 1460, 1400, 1290, 1250, 1210, 972, 930, 791, 710, 663.

## Synthesis of 1a

3-ethylrhodanine (36 mg, 228  $\mu$ mol, 3 eq) and four drops of piperidine were added to a solution of **8a** (100 mg, 0.07 mmol) in 10 mL of CHCl<sub>3</sub> and it was stirred at room temperature for 48 h. The crude was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>:toluene, 7:2.9:0.1). **8a** was obtained as a green-red solid (0.06mmol, 115mg, 95.5 % yield), mp: >300°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.09 (d, 4H, J = 3.9 Hz),

8.95 (d, 4H, J = 3.9 Hz), 7.83 (d, 2H, J = 1.9 Hz), 7.33 (d, 2H, J = 1.9 Hz), 6.64 (s, 2H), 3.73 (d, 4H, J = 5.8 Hz), 3.28 (t, 4H, J = 7.6 Hz), 2.3 (s, 2H), 2.12 (t, 4H, J = 7.28 Hz), 1.95 (s, 2H), 1.75 (s, 6H), 1.58 (s, 16H), 1.45 (s, 12H), 1.23-1.19 (m, 16H), 1.10 (d, 14H, J = 3.95 Hz), 0.97 (s, 4H), 0.85 (t, 4H, J = 6.9 Hz. <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 192.00, 167.12, 151.68, 151.18, 149.32, 148.50, 147.50, 140.06, 134.01, 133.24, 133.03, 130.58, 126.94, 123.79, 122.77, 119.73, 116.27, 104.54, 101.75, 90.42, 39.86, 32.46, 32.18, 31.86, 31.73, 31.12, 30.95, 30.30, 29.73, 29.60, 29.04, 27.69, 23.24, 23.17, 22.92, 14.63, 14.57, 12.61. MALDI-TOF MS (*m*/*z*): calculated for C<sub>88</sub>H<sub>102</sub>N<sub>6</sub>O<sub>2</sub>S<sub>8</sub>Zn: 1594.51; found: 1595.30 (M<sup>+</sup>). FT-IR (ATR) v/cm<sup>-1</sup>: 3670, 3470, 2920, 2850, 2160, 1680, 1560, 1500, 1400, 1320, 1230, 1130, 1010, 877, 785, 729.

### Synthesis of 1b

3-ethylrhodanine (43 mg, 0.26 mmol) and four drops of piperidine, were added to a solution of 8b (50 mg, 0.26 mmol) in 10 mL of chloroform and the solution was stirred at room temperature for 6 hours. Then, the product was purified by chromatography column (silica gel, hexane:CHCl<sub>3</sub>:toluene, 7:2.9:0.1). The final product was a green-red solid (0.08 mmol, 20 mg, 34 % vield), mp: >300°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 9.58 (d, 4H, J = 4.6 Hz), 9.11 (d, 4H, J = 4.6 Hz), 7.79 (s, 2H), 7.72 (d, 2H, J = 3.2 Hz), 7.29 (d, 4H, J = 16 Hz), 7.15 (d, 2H, J = 16 Hz), 4.2-4.14 (m, 4H), 3.2-3.15 (m, 9H), 2.84 (d, 3H, J = 7.3 Hz), 2.67 (t, 6H, J = 6.9 Hz), 2.06-1.98 (m, 9H), 1.56-1.42 (m, 58H), 1.4-1.37 (m, 12H), 1.26 (t, 9H, J = 7.16 Hz), 1.04-0.96 (m, 18H), 0.95-0.89 (m, 12H). <sup>13</sup>C-NMR (100 MHz, THF-d8) δ/ppm: 193.49, 168.14, 153.22, 152.27, 151.43, 149.83, 149.76, 146.08, 143.89, 143.78, 142.19, 139.41, 134.76, 133.78, 132.16, 131.58, 124.87, 123.89, 123.44, 121.06, 120.41, 116.59, 103.27, 103.11, 92.20, 33.66, 33.50, 33.31, 33.21, 33.17, 33.11, 32.98, 32.73, 31.73, 31.39, 30.87, 30.80, 30.75, 30.58, 26.42, 26.29, 26.22, 26.09, 26.02, 25.99, 25.89, 25.80, 25.69, 25.60, 25.49, 25.38, 24.33, 24.21, 24.11, 15.22, 15.20, 15.16, 15.14, 15.04, 13.01. MALDI-TOF MS (m/z): calculated for C<sub>124</sub>H<sub>158</sub>N<sub>6</sub>O<sub>2</sub>S<sub>10</sub>Zn: 2146.89; found: 2146.25 (M<sup>+</sup>). FT-IR (ATR) v/cm<sup>-1</sup>: 2930, 2860, 1700, 1570, 1490, 1460, 1400, 1320, 1240, 1190, 1140, 1070, 957, 850, 789, 708.

## **Device fabrication and characterization**

The BHJ organic solar cells were fabricated using the glass/ITO/ PEDOT:PSS/**1a** or **1b** :PC<sub>71</sub>BM with different weight ratios /Al device architecture. The indium tin oxide (ITO) patterned substrates were cleaned by ultrasonic treatment in aqueous detergent, deionized water, isopropyl alcohol, and acetone sequentially, and finally dried under ambient conditions. The anode consisted of glass substrates percolated with ITO, modified by spin

coating with a PEDOT: PSS layer (40 nm) as a hole transport layer and heated for 10 min at 100° C. Mixtures of **1a** or **1b** with PC<sub>71</sub>BM (total concentration of 12 mg/mL) with weight ratios of 1:05, 1 : 1, 1: 2 and 1:2.5 in THF were prepared and then spin cast onto the PEDOT : PSS layer and dried overnight in an ambient atmosphere. For the **1a** or **1b**:PC<sub>71</sub>BM blend processed with 3 % v/v of pyridine in the THF solvent mixture only the 1:2 weight ratio mixture was used. The approximate thickness of the active layers was 90 nm. Finally, the aluminum (Al) top electrode was thermally deposited on the active layer at a vacuum of  $10^{-5}$ Torr through a shadow mask area of 0.20 cm<sup>2</sup>. All devices were fabricated and tested in an ambient atmosphere without encapsulation. The hole-only and electron-only devices with ITO/PEDOT:PSS/active layer /Au and ITO/Al/ active layer/Al architectures were also fabricated in a similar way, in order to measure the hole and electron mobility, respectively. The current–voltage (J–V) characteristics of the BHJ organic solar cells were measured using a computer controlled Keithley 2400 source meter in the dark and under a simulated AM 1.5G illumination of 100 mW/cm<sup>2</sup>. A xenon light source coupled with the optical filter was used to give the stimulated irradiance at the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured illuminating the device through the light source and the monochromator and the resulting current was measured using a Keithley electrometer under short circuit conditions.

For CuSCN HTL based devices a thin film of the CuSCN (30 nm) layer was spin coated at 2500 rpm for 60 seconds, using diisopropyl sulphide as solvent and annealed at 110° C for 20 minutes and then the active layer was deposited as described above.

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